

EXHIBIT G

POLYMERIC MULTICOMPONENT MATERIALS

An Introduction

L. H. SPERLING

This text is printed on acid-free paper.

Copyright © 1997 by John Wiley & Sons, Inc.

All rights reserved. Published simultaneously in Canada.

Reproduction or translation of any part of this work beyond that permitted by Section 107 or 108 of the 1976 United States Copyright Act without the permission of the copyright owner is unlawful. Requests for permission or further information should be addressed to the Permissions Department, John Wiley & Sons, Inc., 605 Third Avenue, New York, NY 10158-0012.

Library of Congress Cataloging in Publication Data:

Sperling, L. H. (Leslie Howard), 1932–

Polymeric multicomponent materials: an introduction / L. H. Sperling

p. cm.

“A Wiley-Interscience publication.”

Includes bibliographical references and index.

ISBN 0-471-04138-6 (cloth)

1. Polymers. 2. Polymeric composites. I. Title.

QD381.S6348 1998

620.1'92-DC21

Printed in the United States of America

97-6509

10 9 8 7 6 5 4 3 2 1

replacement of the cement, which is recognizable as a composite material containing stones and the like.

2.3.4.3. Foams One case where the nonpolymer phase is clearly deformable involves foams. Here, the gas phase is dispersed in a polymer phase. Two cases must be distinguished: The foam bubble cells may be closed or open. In a closed-cell foam, each gas bubble is isolated. In an open-cell foam, the gas phase forms a continuous phase, as in air filter systems. Seat cushions are often partly open cell and partly closed cell, providing the most comfortable elastic compressive behavior.

2.3.4.4. Wood The structure of wood provides an example of a complex morphology, nature's best. Here, cells of cellulose are dispersed in lignin, a crosslinked polymer resembling a phenolic. The cellulose itself is formed on oriented fibrils, which wind around a porous (hollow) open space, called the lumen. During growth, the lumina contain the organic structure of life. In mature wood, the lumina are interconnected for transport of water and nutrients from the roots to the leaves, and vice versa. These lumina can be filled with polymer for the manufacture of very wear resistant structures, such as knife handles and gymnasium flooring. In this case, the wood serves as the filled phase.

Polymer-impregnated wood is sometimes called a wood-polymer composite (WPC) (31). The monomer, frequently methyl methacrylate, is forced into evacuated wood, and polymerized using heat or irradiation. In general, compressive strength, impact resistance, hardness, and abrasion resistance can be improved. Clearly, such materials are more water and rot resistant.

2.4. POLYMER-POLYMER MISCIBILITY

Up until the early 1970s, it was thought that most polymer blends were substantially immiscible. Further, if there were any mixing taking place, the kinetics of interdiffusion were thought to be so slow as to discourage measurement. Today, we know that polymers and/or their blends must only be above T_g for interdiffusion to be fast enough for measurement. Beginning with the works of McMaster (32,33), Patterson and Robard (34), and others (35-38), well-defined phase diagrams for polymer blends were worked out. To the surprise of most workers in the field, lower critical solution temperatures (LCST) were found in nearly all cases of a blend of two polymers; see Figure 2.6 (39). Thus, early workers attempting to increase miscibility by raising the temperature were going the wrong way, doomed to failure.

Of course, thermodynamic theories all point to some extent of mixing of two components, polymeric or not. This mixing may be great or small, but is always finite.

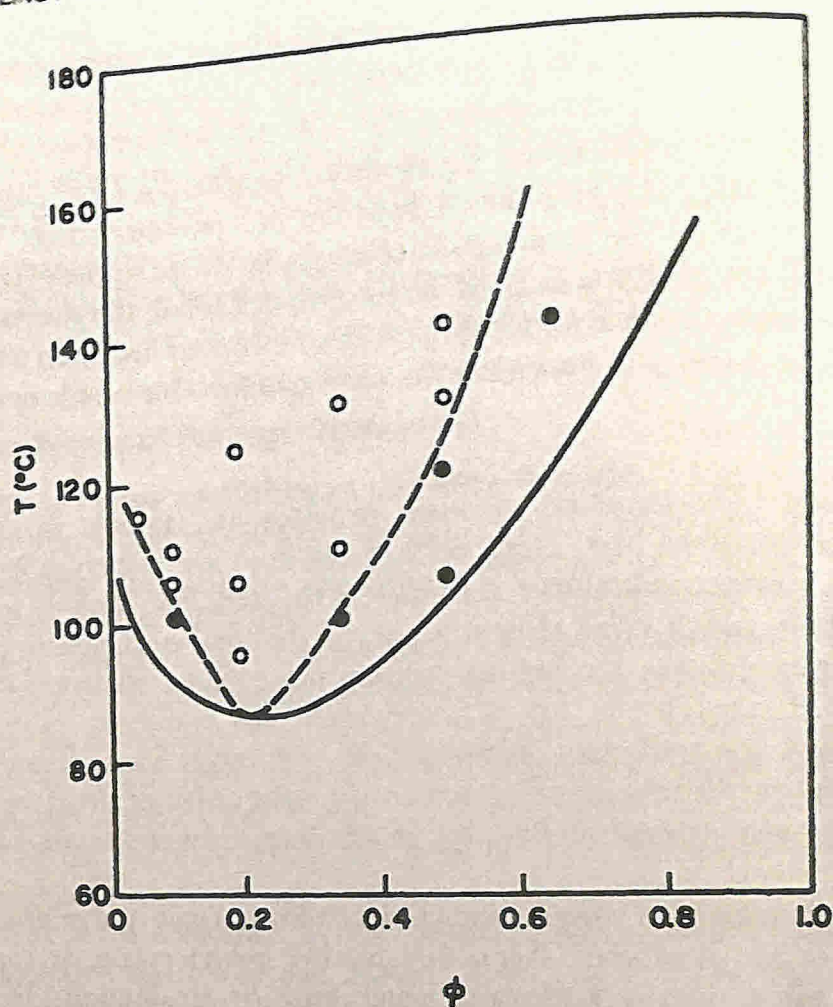


Figure 2.6. Phase separation by spinodal decomposition (open circles) and nucleation and growth (solid circles), as observed under an optical microscope. Solid line, binodal, and dashed line, spinodal.

2.4.1. Phase Diagrams

In general, the shapes of phase diagrams may take many forms. The temperature–volume fraction of several common types of phase diagrams are illustrated in Figure 2.7 (40). Figure 2.7a illustrates total miscibility; Figure 2.7b an upper critical solution temperature (UCST), that is, a temperature above which all compositions are miscible (Figure 2.7c), an LCST; Figure 2.7e illustrates both UCST and LCST conditions; and Figure 2.7d and 2.7f show two cases where the mixture exhibits regions of partial immiscibility.

Phase diagrams are useful for analyzing polymer blend compositions. Consider Figure 2.8, a mixture of polymer I and polymer II, prepared with volume fraction x of polymer II at temperature T . Then, the relative volumes or volume fractions of the two phases can be calculated. Consider that the system has a total volume V . The volumes of the two phases are V_I and V_{II} , and these phases contain volume fractions of polymer II of x_I and x_{II} . Assuming that the

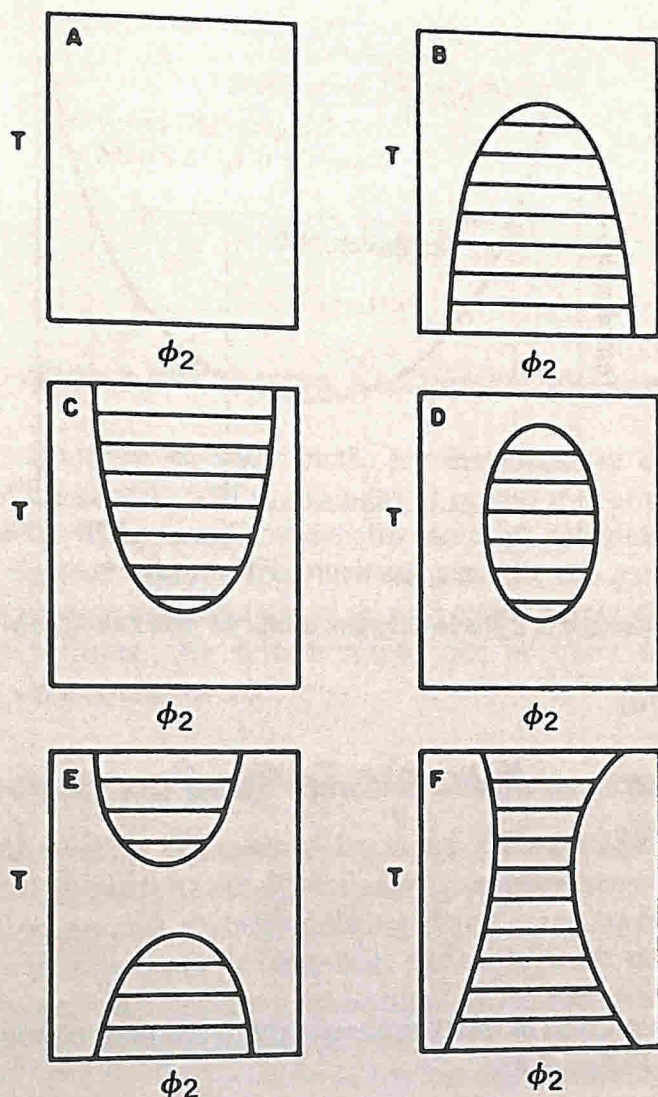


Figure 2.7. Schematics of several types of liquid-liquid temperature-composition phase diagrams. Shaded areas indicate phase-separated regions. $\phi_2 = v_{II}$.

volume changes but little on mixing,

$$V = V_I + V_{II} \quad (2.16)$$

Most polymer phase diagrams are reported in volumes or volume fractions. Weights and weight fractions can easily be substituted. For polymer II in both phases,

$$xV = x_I V_I + x_{II} V_{II} \quad (2.17)$$

Substitution of V from equation (2.16) into equation (2.17) yields

$$x(V_I + V_{II}) = x_I V_I + x_{II} V_{II} \quad (2.18)$$

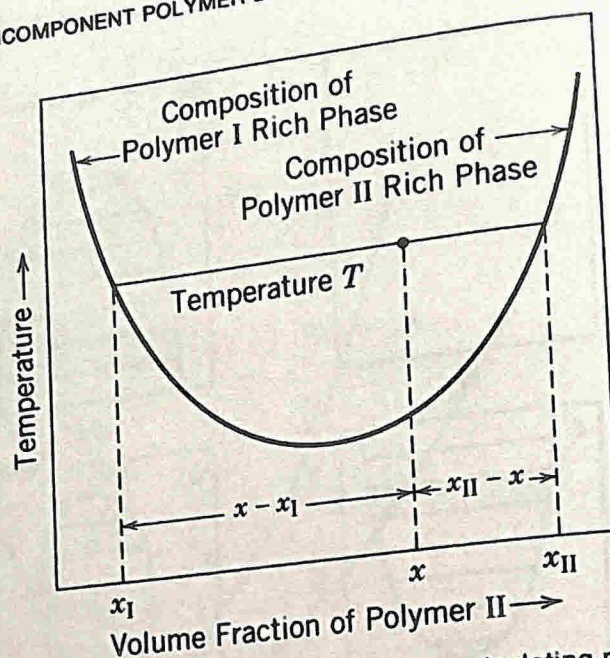


Figure 2.8. Schematic of a phase diagram, useful for calculating phase volumes.

which rearranges to

$$V_I(x - x_I) = V_{II}(x_{II} - x) \quad (2.19)$$

and thus,

$$\frac{V_I}{V_{II}} = \frac{(x_{II} - x)}{(x - x_I)} \quad (2.20)$$

Interestingly, the volumes of the two phases are in the proportion of the two line lengths shown in Figure 2.8.

2.4.2. Model Calculation of Phase Volume Fraction

Using Figure 2.6, let us assume a mix of 60% polystyrene and 40% poly(vinyl methyl ether) (PVHE) at 100°C, and determine the volume fraction of each phase. Then, $x = 0.40$ for polymer II. Using the binodal curve (the outer curve), $x_I = 0.04$ and $x_{II} = 0.48$ from vertical constructions. From equation (2.20),

$$V_I/V_{II} = (0.48 - 0.40)/(0.40 - 0.04)$$

or

$$V_I = 0.22V_{II}$$

Assuming unit volume in equation (2.16),

$$V_I + V_{II} = 1$$